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AVRAMI EQUATION INADEQUACY FOR MODELING THE HDPE ISOTHERMAL CRYSTALLIZATION RATES

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ABSTRACT

The temperature dependence of the crystallization rate of polymers has been related to the classical nucleation and growth process. At temperatures slightly below the melting point, the controlling step is the nucleation process while, with large undercoolings, the rate control shifts toward transport restrictions. With increasing degrees of crystallinity, a shift of the controlling step from nucleation towards transport resistances was also observed, which is frequently associated with a secondary crystallization process. This behavior has also been explained in terms of a separate geometric spreading of the semi-crystalline superstructure followed by an increasing local crystallinity. The Avrami equation is known to be a good model for the first process but rapidly fails with the appearance of a secondary crystallization process and the development of transport resistances. In this work, results of the crystallization rates of HDPE from 118 to 115°C are presented and analyzed of the light of the Avrami equation. It was observed that this model begins to fail with increasing degrees of undercooling and crystallinity. The degree of fitting of the Avrami model, was analyzed processing different ranges of relative crystallinity at four different temperatures, and results are interpreted in terms of the possible rate controlling process. With the Avrami equation a good data fitting at 118ºC was obtained, but it was observed that for increasing degrees of undercooling and increasing degrees of crystallinity the degree of fitting deteriorates. It was found that restricting the use of the Avrami equation within the region of experimental data where it is more likely that the nucleation and the growing process of the semicrystalline superstructure are the controlling steps, very consistent values for Avrami parameters were obtained. Simulation results suggest the presence of a secondary crystallization process for which the Velisaris-Seferis parallel model was found satisfactory.

Keywords: HDPE, crystallization, Avrami model, data fitting, Velisaris-Seferis model.

FALLAS DE LA ECUACIÓN DE AVRAMI EN EL MODELADO DE VELOCIDADES DE CRISTALIZACIÓN ISOTÉRMICA DE PEAD

RESUMEN

La dependencia de la velocidad de cristalización de polímeros ha sido relacionada con los procesos clásicos de nucleación y crecimiento. A temperaturas ligeramente inferiores a la temperatura de fusión, la etapa controlante es el proceso de nucleación mientras que con un subenfriamento grande, el control es transferido hacia restricciones de transporte. Con grados de cristalinidad creciente también se observa un cambio de etapa controlante, entre el proceso de nucleación al comienzo, hacia los procesos de transferencia, lo cual frecuentemente se asocia con la aparición de un mecanismo secundario de cristalización. Este comportamiento también ha sido explicado en función de un crecimiento geométrico de superestructuras cristalinas seguido de un aumento local de crystalinidad. Se sabe que el modelo de Avrami es un buen modelo para el primer proceso pero que rápidamente falla con la aparición del proceso secundario de cristalización y el desarrollo de resistencias crecientes de transporte. En este trabajo se presentan y analizan resultados de velocidades de cristalización del PEAD desde 118 hasta 115ºC usando la ecuación de avrami. El grado de ajuste logrado es analizado procesando diferentes rangos de cristalinidad relativa para cuatro niveles de temperatura, y los resultados se interpretan en términos de las etapas controlantes. A 118ºC el modelo de Avrami ajusta satisfactoriamente los datos experimentales, pero se observa que con grados de subenfriamiento crecientes la calidad del ajuste se deteriora a medida que el grado de cristalinidad aumenta. Se encontró que restringiendo el uso de la ecuación de Avrami a los datos dentro de la región donde el proceso de nucleación, y de crecimiento de la superestructura semicristalina son las etapas controlantes, se obtiene valores consistentes para los parámetros. Los resultados de simulación sugieren la aparición de un mecanismo secundario de cristalización para el cual se encontró satisfactorio el modelo de Velisaris-Seferis.

Palabras clave: PEAD, cristalización, Modelo de Avrami, ajuste de datos, Modelo de Velisaris-Seferis.

INTRODUCTION

The understanding of how, and at what rate, crystalline structures develop during the solidification process of polymeric materials (pure polymers or their mixtures with other polymers or with filling substances), is very important for the development of industrial applications where the final properties of the material are closely related to the crystallization process. This explains why a considerable effort is being dedicated to the development of models that could predict the rate and structures that form during the solidification process, and their dependence upon variables such as temperature, composition and any previous treatment. Among basic models, the Avrami model is probably the most used or well-known (Avrami, 1939). Using appropriate crystallization models (Avrami, 1939; Velisaris & Seferis, 1986; Khanna *et al*., 1988; Dietz, 1981; Malkin *et al*., 1984) with the heat transfer equation, it is possible to predict the temperature and crystalline profiles that arise during the solidification of thermoplastic compounds. These properties can then be related to the final properties of plastic products, specifically their mechanical properties. The knowledge that crystallization processes may determine the final properties of goods manufactured with polymeric materials is a strong motivation for their study.

An important aspect of the crystallization process is the rate at which it takes place, which is interesting from the fundamental point of view of polymer physics and also for the control of unit operations used in the polymer processing. To find crystallization kinetics models that are able to fit experimental data with parameters holding a clear physical meaning would then be interesting.

During the process of crystallization the appearance of changes in the rate controlling resistances or of a secondary crystallization mechanism is likely, to happen in which case the Avrami equation will be partially or fully inadequate, making it necessary to consider alternative and more complex models. Following this idea, the isothermal crystallization kinetics of samples of High Density Polyethylene (HDPE) were studied at four temperatures, and results were analyzed using the models of Avrami (Avrami, 1939), Velisaris-Seferis Parallel[VS (Parallel)] and Velisaris-Seferis Serial [VS (Serial)] (Velisaris & Seferis, 1986).

The Avrami equation for relative crystallinity is:

$$\theta(t) = 1 - \exp\left(-kt^{n}\right) \tag{1}$$

while the Velisaris Seferis parallel is:

$$\theta(t) = w_1(1 - \exp(-k_1(T)t^{n1})) + w_2(1 - \exp(-k_2(T)t^{n2})) \tag{2}$$

and that of Velisaris-Seferis serial is:

$$\frac{1}{\theta(t)} = w_1\left(\frac{1}{1-\exp\left(-k_1(T)\,t^{n1}\right)}\right) + w_2\left(\frac{1}{1-\exp\left(-k_2(T)\,t^{n2}\right)}\right) \tag{3}$$

where:

$$\theta(t) = \frac{X(t)}{X_\infty} \tag{4}$$

is the relative crystallinity at time «t».

EXPERIMENTAL

Experiments were carried out using the homopolymer HDPE (MFI = 4.88 g/10 min at 190ºC, Mw=77456 g/mol, ρ=0.94 g/cc) supplied by Chemical Container Andina. Isothermal crystallization runs were performed in a Mettler Toledo DSC model 821, using nitrogen as the dragging gas, and standard flat-surface aluminium capsules. Each sample was first kept over its melting temperature, and maintained at that temperature during five minutes so as to erase any previous thermal history. Immediately after this point, samples were cooled at the maximum rate allowed by the equipment to the desired crystallization temperature, which was maintained long enough to ensure that the crystallization process was completed. The crystallization temperatures studied were 118, 117, 116 and 115ºC.

RESULTS AND DISCUSSIONS

Normalized thermograms are shown in Figure 1. As can be seen, within the temperature windows explored, the rate of crystallization increases with decreasing temperatures, which means shorter times to reach complete crystallization as the sub-cooling gets higher. Additionally it can be seen that the induction time for crystallization increases with increasing temperatures.

Figure 2 shows the experimental relative crystallinity evolution with time. As can be seen, the time needed to reach 50% of relative crystallinity ($t^{½}$) decreases rapidly with decreasing crystallization temperatures from 108(s) at 118ºC to 20 (s) at 115 ºC.

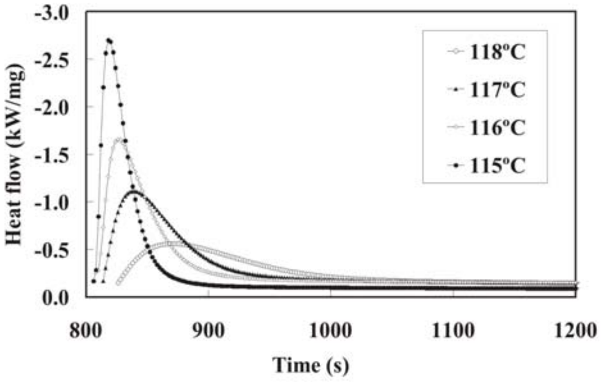

Figure 1. HDPE isothermal crystallization exotherms.

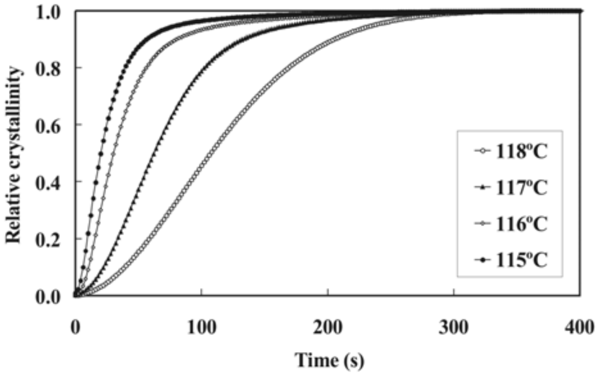

Figure 2. Experimental relative crystallinity for HDPE.

The HDPE isothermal crystallization kinetics is usually modeled using the Avrami equation (Avrami, 1939; Kamal & Chu, 1983; Albano *et al.*, 2000), whose parameters are evaluated by linearization of experimental data, plotting the function:

$$\ln\left(-\ln\left(1-\theta(t)\right)\right) \text{ versus } \ln(t) \qquad (5)$$

Following this, it was observed that the correlation index decreases with decreasing crystallization temperature, what could mean a change in the rate controlling step, or in the crystallization mechanism or both at the same time. Parameters evaluated by this procedure are afterward correlated as a function of the temperature.

The precision of Avrami's parameters obtained using the described graphical procedure strongly depends on the quality of the experimental data at low values of relative crystallinity. In order to achieve a better approach to parameter evaluation, in this work models were fitted to experimental data following a different procedure. It consists in defining an objective function such as:

$$F_{objec.} = \sum_i \left[\theta(t_i)_{exp.} - \theta(t_i)_{model}\right]^2 \qquad (6)$$

which is then minimized using a non linear regression method.

Assuming for parameters of the model an adequate relationship with the temperature, this method can be used to process simultaneously all data of all exotherms. In this case, it was considered that the specific crystallization rate constant follows the Arrhenius law, and in order to accelerate convergence, it was rewritten as:

$$k_i = k_{T_m} \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_i} - \frac{1}{T_m}\right)\right] \qquad (7)$$

where:

$$k_{T_m} = k_o \exp\left(-\frac{E_a}{RT_m}\right) \qquad (8)$$

with $T_m = 389.6$ K [8].

Every model, unless it is completely empirical, has parameters with some physical meaning related to the basic assumption made during their development. These parameters will preserve their physical meaning as long as those basic assumptions can be maintained during the crystallization process.

In the case of the Avrami equation, the parameter «n» is related to the geometry and «k» to the growing rate of crystals, and this physical meaning can be sustained as long as the following basic assumptions are approximately valid: a) the linear growth velocity of spherulites is constant, b) the volume where the crystallization takes place is infinite compared to the crystal size, c) there is not a volume shrinkage, d) the nuclei are randomly distributed, e) the nucleation density and rate are constant and f) the homogeneous and the heterogeneous kind of nucleation do not take place simultaneously (Hinrichs *et al.*, 1996). These assumptions can be fairly accepted as valid at the beginning of the crystallization process but some of them will surely fail from a certain point of relative crystallinity and up. Sometimes, as for some of our experiments, the Avrami equation is able to approach satisfactorily experimental data over almost all the range of relative crystallinity but, when this is the case, the model should be regarded as an empirical one, parameters can no longer be associated with a physical meaning, and it could be considered as a model failure. To clarify this point, our experimental data was modeled with the Avrami equation with parameter values obtained doing a non-linear regression against the whole set of experimental data (from the beginning to the end of each crystallization experiment, and for all crystallization temperature) in one case, and using only a subset of experimental results (from the beginning to the position of the exotherm pick and for all crystallization temperatures) in the other. The sum of squared differences between experimental and simulated data for the whole set of experimental data, gave a value of 0.381 using Avrami parameters obtained by regression over the whole set of experimental data, and of 0.647 with parameters obtained by regression using only the subset of data. Applying an F test with a confidence limit of 95% it was found that the whole set and the subset do not belong to the same family. For the subset it can be accepted that the basic assumptions for the Avrami model are fulfilled, and so the parameters preserve their physical meaning. Instead, those obtained using the whole set of experimental data must be regarded as fitting parameters without an attached physical significance. In this case, the Avrami model can be seen perhaps as a good empirical model that fails to give some physical meaning to the parameters. This means that at a certain point of the crystallization process, a gradual change in the controlling forces or a secondary crystallization process appears.

Experimental and simulated results are shown in Figure 3. It can be seen that the Avrami equation is unable to satisfy the whole set of experimental data, and that the difference is more noticeable with increasing sub-cooling. Soon after the nucleation process, crystals can grow almost without touching between them. Thus, at the beginning of the crystallization process the Avrami equation should simulate experimental data quite well, preserving the physical meaning of parameters, but as the crystallite size increases the environment of each one of this crystallite changes as well, and accordingly parameters values will change too, and will lose their physical meaning. Figure 4 shows differences between the simulated results with Avrami (Subset) and the corresponding experimental value which, ignoring the gray error band induced by the experimental startup procedure, are clearly meaningful. The difference suggests the onset of changes in the values of parameters due to changes in the driving forces or in the controlling step, the appearance of a secondary crystallization phenomenon, or to all of them at the same time.

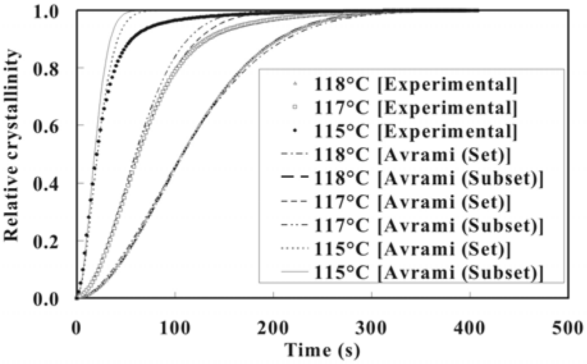

Figure 3.- Experimental and simulated relative crystallinity.

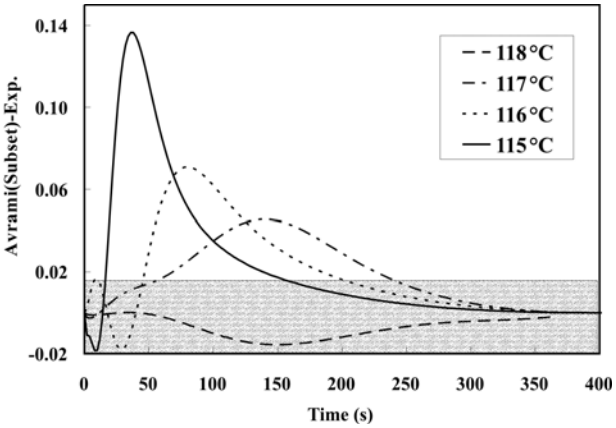

Figure 4. Relative crystallinity difference: Avrami (Subset) model minus experimental data.

Another way to analyze what has been suggested by Figure 4 is shown in Figure 5 where meaningful differences between simulated values using parameters obtained with the subset of experimental data, and those simulated using parameters obtained with the complete set of data are presented. A comparison of both figures shows that it is not possible to simulate the full set of data for each isotherm with a unique set of parameters.

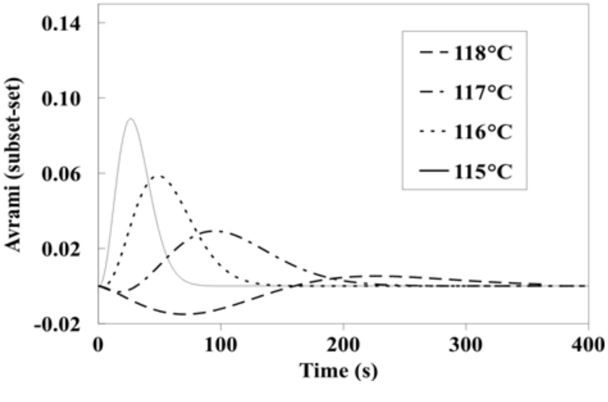

Figure 5. Relative crystallinity differences between Avrami (Subset) and Avrami (Set).

According to these results, the full set of experimental data was fitted in the way previously described, but using the Velisaris-Seferis serial [VS (Serial)] and parallel [VS (Parallel)] models (Velisaris & Seferis, 1986), which incorporate a secondary crystallization process. Assuming that the weight factor «w_1» is a linear function of temperature, and that the importance of the primary crystallization process decreases as the temperature gets lower, it was stated that they obey the following relationship:

$$w_1 = a + b\left(T_f - T\right) = 1 - w_2 \qquad (9)$$

subject to the restriction that $w_1+w_2=1$, with both fractions defined positive.

Table 1 shows the sum of the squared differences obtained with each one of the models. Considering the degree of freedom for each one, the values for the ratio of these differences, and the tables of F distribution, it is possible to discriminate in favour to the Velisaris-Sefelis parallel model with a confidence level even higher than 95%.

Table 1. Objective function values and their ratio.

Model	$F_{objective}$	F/F_{minor}
Avrami (Set)	0.381	5.603
Avrami (subset)	0.647	9.515
Avrami (linear)	0.860	12.647
VS (Serial)	0.804	11.824
VS (Parallel)	0.068	1.000

Results clearly show that the Avrami equation fails to model the full set of experimental data, and also suggest the presence of a secondary crystallization process which occurs simultaneously with the primary crystallization process.

Some simulation results of relative crystallinity using the Velisaris-Seferis parallel models are shown simultaneously with experimental data, and simulated results using the Avrami (Subset) and Avrami (Set) models, in Figures 6, 7 and 8.

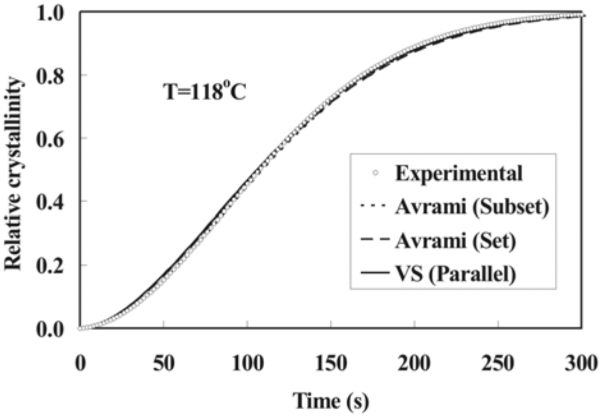

Figure 6. Experimental and simulated curves at 118°C.

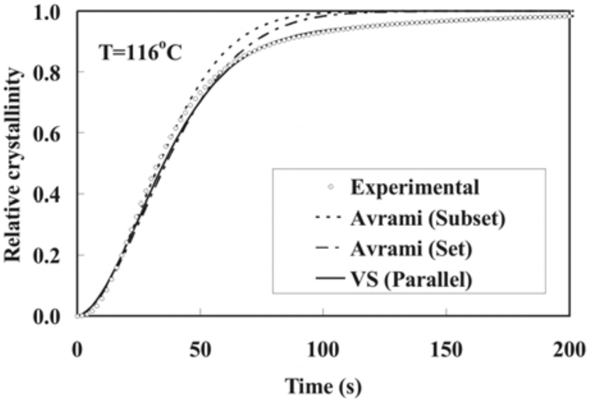

Figura 7. Experimental and simulated curves at 116°C.

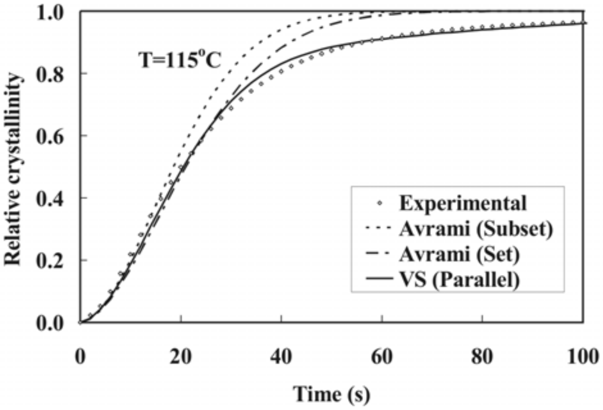

Figura 8. Experimental and simulated curves at 115°C.

Simulated results using the Avrami (Set) model approach to the experimental data better than those obtained using the Avrami (Subset) model what agree with the data reported in table 1. Both models are identical from the mathematical point of view, but their parameters are different and as it was explained before, only those corresponding to the subset are clearly associated with the Avrami basic assumptions. Applying the F test (Himmelblau, 1970) with a confidence level of 95% to both models, it can be concluded that both set of parameters are different, what means that there is a meaningful change in the controlling forces that govern crystallization with increasing relative crystallinity. Nevertheless, plotting unsatisfied differences between the Avrami (Subset) predictions and experimental data (Figure 4) and those between Avrami (subset) and Avrami (Set) models (Figure 5), the need for a model capable of taking into account a secondary crystallization process is evident. Figure 6 shows that the Avrami (set), Avrami (Subset), and the Velisaris-Sefelis (parallel) models simulate equally well experimental data at 118°C, what means that the controlling crystallization mechanism is nucleation. As shown in Figures 7 and 8, with decreasing temperatures there appear differences between models which can be attributed to changes in transport resistances, and to the appearance of a secondary crystallization process. In order to better appreciate the differences between the models, Figures 6, 7 and 8 show the most sensitive region magnified. The Avrami's model inadequacy to simulate the whole set of data when compared with Velisaris-Seferis (Parallel) is clearly shown. This can be seen better when comparing Figure 9, which shows unsatisfied differences between the Velisaris-Seferis (Parallel) and experimental data, with Figure 4. Differences shown in Figure 9 are much smaller than those shown in Figure 4. The oscillations around the zero are mainly attributed to perturbation induced by the experiments start-up procedure, making a further improvement in the model prediction almost impossible.

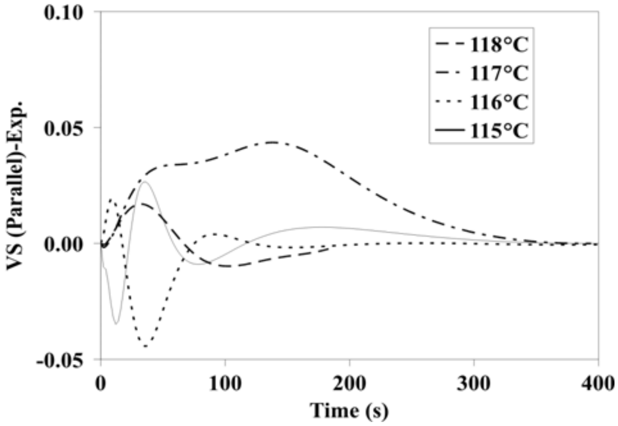

Figure 9. Relative crystallinity difference: V-S(Parallel) minus experimental data.

These results confirm the presence of a secondary parallel crystallization process but they do not exclude the possibility of a simultaneous change in the controlling crystallization resistances, as was suggested by the comparison of simulated results obtained using the Avrami (Set) model with those obtained with the Avrami (Subset) model.

CONCLUSIONS

When analyzing isothermal crystallization data of HDPE samples at different temperatures, it has been found that the Avrami model is not capable of representing experimental results without losing the physical meaning of its parameters, and is strongly suggested the convenience of considering a possible change in the governing driving forces with increasing values of the crystallinity, and perhaps to consider the appearance of a secondary crystallization mechanism or both phenomena at the same time

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NOMENCLATURE

K	Specific crystallization constant for Avrami's model, equation (1)
E_a	Apparent activation energy
k_1	Specific crystallization constant for V-Sp, equation (2) and V-Ss, equation (3)
k_2	Specific crystallization constant for V-Sp, equation (2) and V-Ss, equation (3)
k_{Tm}	Specific crystallization constant at the averaged temperature T_m
a,b	Origin and slope in equation (9)
k_o	Frecuency factor
n	Exponent in equation (1)
n_1	Exponent in equation (2) and (3)
n_2	Exponent in equation (2) and (3)
R	General gas constant
T	Temperature
T_m	Average of the used experimental temperatures
T_f	HDPE melting temperature
t	Time
$t^{½}$	Time when è(t)=0.5
X	Absolute crystallinity
X_i	Absolute crystallinity at time t_i
$X_{»}$	Absolute crystallinity at infinite time
s	Second (unit of time)
w_1, w_2	Weight factors in equation (2) and (3).
$\theta(t)$	Relative crystallinity at time t, equation (4) (dimensionless)

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